

## The inhibitive action of Pistacia lentiscus as a potential green corrosion inhibitor for mild steel in acidic medium

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### Abstract

The aim of present work is to test the effect of the extract (PLE) and the essential oil (PLO) of Pistacia lentiscus as a potential green corrosion inhibitors for acidic media using weight loss measurements and electrochemical techniques (potentiodynamic polarization curves, and electrochemical impedance spectroscopy) in the presence of different concentrations of PLE & PLO ranging from 0.25 to 2 g/L. The inhibition efficiency was found to increase with increasing inhibitor concentration up to maximum 81.2% and 92.1% for PLO and PLE at 2g/L, respectively. Potentiodynamic polarization showed that PLE and PLO act as mixed type inhibitors. Nyquist plots show that the efficiency of inhibition increases with increasing concentration of PL and the increased charge transfer resistance. Adsorption of PLO and PLE on the steel surface followed a Langmuir's isotherm and the thermodynamic parameters were determined and discussed.

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## 1. Introduction

*Pistacia lentiscus* L. is a dioecious evergreen shrub member of the *Anacardiaceae* family. It is native throughout the Mediterranean region, from Morocco and Iberian peninsula in the west through southern France and Turkey to Iraq and Iran in the east. It is also native to the Canary Islands. Moreover, it is found in the flora of many Mediterranean regions. In Morocco, *P. lentiscus* L. occurs in various regions, particularly in the mid-west of the Rif Mountains [1]. The aerial parts of *P. lentiscus* L. has traditionally been used in the treatment of hypertension and possesses stimulant and diuretic properties [2]. Mastic gum from *Pistacia* has been used by traditional healers for the relief of upper abdominal discomfort, stomachaches, dyspepsia and peptic ulcer [3]. Several studies have also reported that essential oil from aerial parts of *P. lentiscus* L. possesses appreciable biological properties such as antifungal, antibacterial and antimicrobial [4-8]. Recently, several researchers have been focused toward the investigation of natural products for the discovery of active compounds with antioxidant properties that can be applied to the food industry. These compounds can be also used such as additives or preservatives compounds in order to replace the synthetic chemicals. On the other hand, there has been growing interest in the research of the compounds named green inhibitors. These compounds are eco-friendly, ecologically acceptable and biodegradable. Plant extracts have become important as readily available and renewable source of materials [9-12]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful uses of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by several workers [13-17]. The protection of metal and its alloys from corrosion is of paramount importance for corrosion scientists. Many successful endeavours have been made to deliver methods for controlling the threat of corrosion. Although, metal finds broad spectrum of technological applications, its poor corrosion resistance in acids [18-20] restrains its usefulness. Acid solutions are frequently used in industrial processes such as pickling, cleaning, and descaling, and thus chances of mild steel corrosion is particularly high in these industrial processes [21-23]. Several methods are used to control the corrosion process but application of inhibitors has been proven to be most practical and efficient for this purpose. The present work continues to point on the application of plant extracts for metallic corrosion control. Furthermore, it reported an attempt to use electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss method to investigate the inhibitive action of *Pistacia lentiscus* as a potential green corrosion inhibitor for mild steel in acidic medium and the nature of adsorption on the mild steel surface.

## 2. Experimental Section

### 2.1. Material preparation and solutions

The chemical composition of mild steel used (in wt%) was 0.09 % P, 0.38 % Si, 0.01 % Al, 0.05 % Mn, 0.21 % C, 0.05 % S, and balance Fe. The aggressive media was prepared by diluting a Merck analytical commercial grade 98 %  $\text{H}_2\text{SO}_4$  with deionized water. All experiments were carried out in 0.5M  $\text{H}_2\text{SO}_4$  solution in the absence and presence of different concentrations (0.25, 0.5, 1 and 2 g/l) of PLO and PLE. Clevenger-type apparatus was used to extract the essential oil from the dried aerial parts according to the method recommended in the European Pharmacopoeia [24]. Oils obtained were treated with anhydrous sodium sulfate and then stored to future analysis. Stock plant extract was prepared by an aqueous maceration and was performed on 0.2 g of plant with 100 mL of 0.5M  $\text{H}_2\text{SO}_4$  solution for 24 h. After filtration, the extract was recovered.

## 2.2. Determination of total phenolic content of extract

The total content of phenolic extract of *P. lentiscus* was determined according to the colorimetric method of Folin-Ciocalteu reagent [25]. 1 ml aliquot of Folin-Ciocalteu reagent (10%) and 0.2 ml of aqueous extract was prepared. The mixture was kept in the dark for 4 min. then, 0.8 ml of  $\text{Na}_2\text{CO}_3$  (75 g / L) was added to the mixture. After 30 min of incubation, the absorbance was measured at 765 nm.

Gallic acid was used as standard and the results were expressed as mg gallic acid (GAE)/g *P. lentiscus* (the equation regression was  $y = 0,0052.x + 0,0258$ ,  $r^2 = 0,9957$ ).

## 2.3. Estimation of total flavonoids content of extract

In order to measure the flavonoids contained in the extract of *P. lentiscus*, aluminum chloride colorimetric was used as known method [26]. The mixture of analyses was contained 1 ml of sample (1 mg/mL) and 1 mL of  $\text{AlCl}_3$  (2% in ethanol). The mixture was kept at room temperature for 10 min in dark. Then, the absorbance was measured at 430 nm. Quercetin was used to build the calibration curve ( $y = 0,0344.x + 0,0088$ ,  $r^2 = 0,991$ ). Then, the flavonoids content were expressed as mg quercetin (QE)/g *P. lentiscus*.

## 2.4. Determination of total flavonols content of extract

According to aluminum chloride method [27], flavonols content was measured using a UV/Vis spectrophotometer at the wavelength 415 nm against a calibration curve of quercetin ( $y = 0,008.x - 0,016$ ,  $r^2 = 0,998$ ). The assay is performed in a test tube. 2.8 ml of distilled water, 0.1 ml of  $\text{AlCl}_3$ , 0.1 ml of  $\text{CH}_3\text{CO}_2\text{K}$  (1 M), 0.5 ml of the extract are mixed, then incubated in the shade at room temperature for 30 minutes. The flavonols content were expressed as mg quercetin (QE)/g *P. lentiscus*.

## 2.5. DPPH radical scavenging activity

This study designed to assess the scavenging capacity of the bioactive compounds of plant extract against the stable 1,1-diphenyl-2-picryl hydrazyl radical (DPPH) using the known method named DPPH free radical scavenging assay [28]. Various concentrations of the ethanolic solution of the aqueous extract have been prepared ranging from 5 to 100  $\mu\text{g/mL}$ . Analysis solution was contained 1.9 mL of DPPH solution and 0.1 ml of aqueous extract. The samples were shaken vigorously and kept in a dark for 30 min. Then, their absorbance was read at 517 nm using a UV/Vis spectrophotometer. The scavenging activity DPPH radical was expressed as percentage DPPH discoloration by the following formula:

$$\left[ (A_{\text{blank}} - A_{\text{sample}}) / A_{\text{blank}} \right] \times 100 \quad (1)$$

Where,  $A_{\text{sample}}$  is the absorbance of the solution containing the sample at 515 nm, and  $A_{\text{blank}}$  is the absorbance of the DPPH solution. The  $\text{IC}_{50}$  values were calculated as the concentration of extract causing a 50% inhibition of DPPH radical.

## 2.6. Gravimetric analysis

Gravimetric measurements were carried out according to the standard methods [29]. Specimens used with dimensions of  $2.5 \times 2.5 \times 0.5 \text{ cm}^3$  were abraded with series of emery papers SiC up 1200 grade and then they have been washed with distilled water, degreased with acetone, dried and weighed accurately. After immersion period (6h), the mild steel specimens were carefully washed in double-distilled water, dried and

then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss is reported.

## 2.7. Electrochemical measurements

Electrochemical measurements experiments were conducted using an electrochemical measurement system Volta lab (Tacussel- Radiometer PGZ 100) controlled by a PC supported by Voltamaster.4 Soft-ware. Three cylindrical electrodes made of Pyrex glass were used as measuring cell. A saturated calomel electrode (SCE) was used as reference, platinum electrode (CE) as counter-electrode with surface area of  $1\text{ cm}^2$  and the working electrode (WE) was of mild steel. Only  $0.2\text{ cm}^2$  of cross section of this electrode was allowed to contact the aggressive solution. The working electrode was immersed in test solution for 30 minutes to establish a steady state open circuit potential ( $E_{\text{corr}}$ ). All potentials are reported vs. SCE. All electrochemical tests have been performed in aerated solutions at 303 K. The EIS experiments were conducted at the steady state of open circuit potential, in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, after 30 min of immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. Before recording the curves the test solution is de-aerated in magnetically stirred for 30 min in the cell with nitrogen.

## 3. Results and discussion

### 3.1. *Pistacia lentiscus* oil analysis

Results obtained by GC-MS chemical analysis of the essential oil of *P. lentiscus* are shown in Table 1. In total, 37 compounds were identified, which accounted for 83.3% of the total oil. The essential oil was characterized by high amounts of Limonene (32.7%). The other main constituents were  $\alpha$ -Pinene (5.5%), Terpinen-4-ol (5.1%). The 7 other compounds are reported in low amounts. It should be noticed that several studies have been published on chemical composition of *P. lentiscus*. Among these studies, the study performed by Aouinti et al. [30] in Eastern Morocco: Saïdia ( $35^{\circ}05'N$ ,  $02^{\circ}14'W$ ), showed that Limonene (18.9%) was the elevated individual compound in *P. lentiscus* oil followed by  $\alpha$ -Pinene (13.9%),  $\beta$ -caryophyllene (6.9%),  $\alpha$ -terpineol (6.78%) and Terpinen-4-ol (5.5%). Other research has reported the chemical composition of *P. lentiscus* essential oil from Tuscany (Italy) which was performed by GC/MS contained  $\alpha$ -pinene (16.1–25.3 %), limonene (6.6–12.3%), terpinen-4-ol (7.6–12.7%) and germacrene-D (9.6–14.3 %) as major components used on data obtained in the present work and others, we note that there's a considerable difference in the chemical composition of *P. lentiscus* oil. In the fact this difference can be attributed to several factors as the period of harvested, the period of sunshine, the nature and the composition of the ground [31].

**Table1** Essential oil components of *Pistacia lentiscus*

<i>Composés</i>	<i>IL</i>	<i>Ir /apol</i>	<i>Ir /pol</i>	<i>%</i>
$\alpha$ -Pinene	936	931	1026	5.5
Camphene	950	943	1062	0.3
Sabinene	973	966	1123	0.4
$\beta$ -Pinene	978	971	1107	1.2
Myrcene	987	982	1155	1.9
p-Cymene	1015	1014	1271	2.4
Limonene	1025	1023	1199	32.7
Linalol	1086	1085	1544	1.0
cis-p-Mentha-2.8-dien-1-ol	1113	1118	1644	0.4
Terpinen-4-ol	1164	1166	1600	5.1
$\alpha$ -Terpineol	1176	1175	1692	2.1
trans-Carveol	1200	1198	1826	0.5
cis-Carveol	1210	1212	1843	0.4
Carvone	1214	1217	1729	0.5
Geraniol	1235	1234	1843	0.3
Undecan-2-one	1273	1275	1598	0.6
$\alpha$ -Copaene	1379	1380	1495	0.7
$\beta$ -Elemenene	1389	1390	1592	0.7
trans-Caryophyllene	1421	1421	1565	4.8
$\alpha$ -Humulene	1455	1452	1670	1.0
Alloaromadendrene	1462	1459	1646	0.4
g-Murolene	1474	1473	1690	1.4
$\alpha$ -Murolene	1496	1495	1719	0.9
$\beta$ -Bisabolene	1503	1502	1713	0.2
g-Cadinene	1507	1508	1758	0.3
Calamenene	1517	1512	1829	0.6
$\delta$ -Cadinene	1520	1517	1758	1.2
Spathulenol	1572	1569	2116	0.7
Caryophyllene oxyde	1578	1572	1976	4.8
epoxyde Humulene II	1602	1595	2030	0.6
epi-Cubenol	1623	1615	2059	1.5
tau Cadinol	1633	1629	2181	2.3
Hinesol	1632	1632	2190	1.1
Cubenol	1630	1633	2030	0.7
$\alpha$ -Cadinol	1643	1641	2225	2.9
$\alpha$ -Bisabolol	1673	1669	2210	0.6
Benzyl benzoate	1730	1727	2615	0.6
TOTAL			83.3	

### 3.2. Determination of total phenolic content (TPC), total flavonoids (TF) and flavonols

Phytochemicals in plant extracts have exhibited antioxidant properties and they were reported to be reducing agents, hydrogen donors, singlet oxygen quenchers and metal chelating agents. These properties will allow it to be excellent antioxidants [32-34]. The results listed in Table 2 depict that the aqueous extract contain appreciable amounts of phenolic compounds, flavonoids and flavonols. We can remark also that *P. lentiscus* leaves are poor in flavonoids.

**Table 2:** Phenolic compounds of aqueous extract of *P. lentiscus*

Extrait	TPC <sup>(a)</sup>	TF <sup>(b)</sup>	Flavonols <sup>(b)</sup>
PLE	62,9 ± 4,8	3,9 ± 0,1	10,8 ± 0,8

All the values are mean ± SD; SD: standard deviation

<sup>(a)</sup> (mg GAE/g powder).

<sup>(b)</sup> (mg QE/g powder).

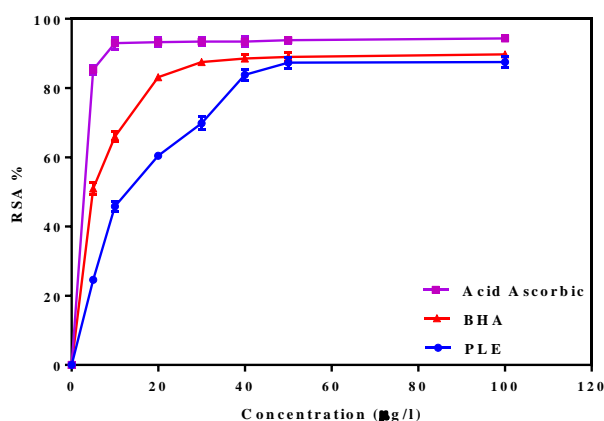
### 3.3. Scavenging activity of DPPH radical

Radical scavenging activity is frequently used to evaluate the capacity to scavenge the “stable” free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH). It is practice and accurate method to titrate oxidizable groups of natural or synthetic antioxidants. This method is based on the spectrophotometric measurement of the color of the DPPH solution. Therefore, in presence of an antioxidant in the medium, the deep violet color is decreased. Thus, the antioxidant compounds have neutralized the free radicals (DPPH).

The results of extract aqueous and positive control (acid ascorbic) are presented in Table 3.

**Table 3:** DPPH radical scavenging activity of aqueous extract of *P. lentiscus*

Sample	Scavenging ability (% , Mean ± SD), concentration (µg/mL)						
	5.0	10.0	20.0	30.0	40.0	50.0	100.0
PLE	24,6 ± 0,8	45,8 ± 1,4	60,4 ± 0,8	69,8 ± 1,9	83,7 ± 1,6	87,3 ± 1,6	87,5 ± 1,7
BHA	51,0 ± 1,6	65,9 ± 1,5	83,1 ± 0,9	87,5 ± 0,1	88,5 ± 1,0	89,0 ± 1,2	89,8 ± 0,7
Acid ascorbic	85,3 ± 1,3	93,0 ± 1,7	93,2 ± 1,2	93,4 ± 1,1	93,4 ± 1,5	93,8 ± 1,0	94,3 ± 1,0



**Figure 1.** Radical Scavenging Activity of PLE

Fig 1 shows that radical scavenging activity (RSA, %) increased with increasing amount of the extract and positive controls (acid ascorbic and BHA). From the IC<sub>50</sub> value of aqueous extract (13.10 µg/mL) we conclude that his scavenging activity is lower than that exhibited from acid ascorbic (2.82µg/mL) and that of BHA (6.80 µg/mL).

### 3.4. Weight loss tests

The gravimetric measurement is a practical method for supervising the corrosion rate of steel in the absence and the presence of various concentrations of PLE and PLO after 6 h of immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 308 K. The following equation was used to determine the inhibition efficiency  $\eta_{WL}$  (%):

$$\eta_{WL}(\%) = \left(1 - \frac{W'_{corr}}{W_{corr}}\right) \times 100 \quad (2)$$

Where  $W_{corr}$  and  $W'_{corr}$  are the values of corrosion rate of mild steel in uninhibited and inhibited solutions, respectively.

**Table 4:** Corrosion parameters data collected from weight loss measurements for mild steel in presence and absence of PLE & PLO in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 308 K

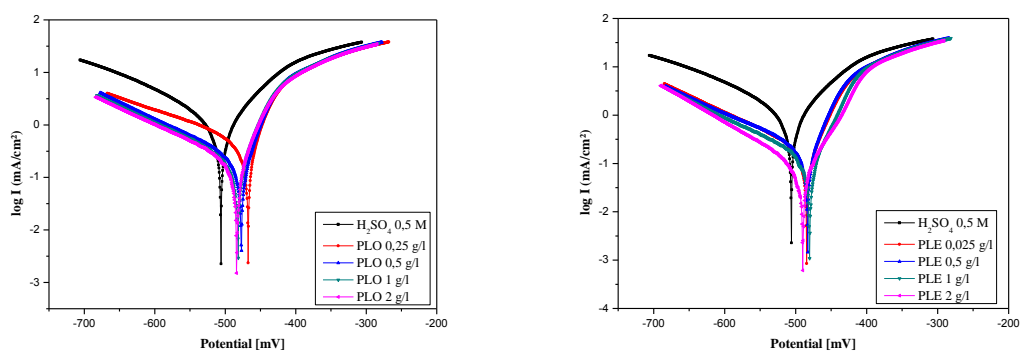
Compounds	Conc. (g/l)	$W_{corr}$ (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	$\eta_{WL}$ (%)
Blank	0.5	0.520	-
PLO	0.25	0.218	58.0
	0.5	0.109	78.8
	1	0.104	79.8
	2	0.097	81.2
	0.25	0.123	76.1
PLE	0.5	0.123	76.1
	1	0.087	83.2
	2	0.065	87.3

Clearly, examination of the collected results listed in Table 4, reveals that corrosion rate ( $W_{corr}$ ) decreases with gradually increasing in inhibitor concentrations in both cases (PLO and PLE) and the inhibition efficiencies increases to achieve 81.2 % and 87.3 % for PLO and PLE at 2g/L, respectively. On the other hand, the high efficiency values indicate that these compounds within inspection are efficient inhibitors of mild steel in test solutions.

### 3.5. Polarization curves

Polarization study is a suitable technique in studying corrosion mechanisms; it has been performed in order to get information about the kinetics of the anodic and cathodic reactions. The polarization curves were obtained in the potential range from -800 to -200 mV(SCE) with 1 mV s<sup>-1</sup> scan rate. The representative potentiodynamic polarization curves of steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence and the absence of the tested inhibitors are shown in Fig. 1.





**Figure 2.** Polarisation curves of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> for various concentrations of *P. lentiscus* oil and its extract.

Corrosion parameters such as  $I_{corr}$ ,  $E_{corr}$ ,  $\beta_c$  and  $E_p$  % obtained from curves are summarized in Table 5.

**Table 5** Electrochemical parameters and inhibition efficiency values for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of PLE and PLO respectively

Compounds	Conc. (g/l)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{corr}$ (mV)/SCE	$b_c$ (mV/dc)	$E_p$ (%)
blank	0.5	901	-506	-194	-
PLO	0.25	439	-467	-208	51
	0.5	205	-477	-154	77
	1	194	-481	-157	78
	2	182	-483	-158	79
PLE	0.25	176	-484	-142	80
	0.5	166	-483	-145	81
	1	107	-479	-132	88
	2	80	-489	-116	91

Based on data given in Table 5, the inhibition efficiency  $E_p$  (%) was calculated using the following equation [35]:

$$E_p \% = \left( 1 - \frac{I'_{corr}}{I_{corr}} \right) \times 100 \quad (3)$$

Where  $I_{corr}$  and  $I'_{corr}$  are respectively, the corrosion current densities in uninhibited and inhibited acid mediums. They were calculated from the intersection of cathodic and anodic Tafel lines. It is well marked from values given in Table 5, that  $I_{corr}$  values have been diminished distinctly from 901  $\mu\text{A}/\text{cm}^2$  for the blank to 182 and 80  $\mu\text{A}/\text{cm}^2$  in presence of PLO and PLE at the highest concentration (2 g/L), respectively. This may be due to the adsorption of inhibitors on mild steel/acid interface. The obtained efficiencies ( $E_p$  %) indicate that *P. lentiscus* inhibitors act as an effective inhibitors. The values of  $E_p$  (%) increase with the inhibitors concentration to reach 79.7% and 91.1% for PLO and PLE, respectively at 2 g/L. In addition, the adding of inhibitors tested to the aggressive media modifies the cathodic Tafel slope ( $\beta_c$ ), then the mechanism of the process is affected and Inhibit both cathodic and anodic reactions. These results

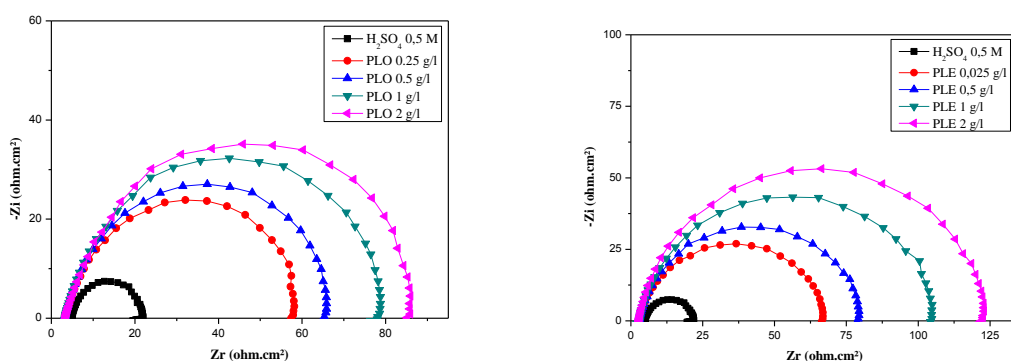


reveal that the presence of inhibitors reduces the anodic dissolution of mild steel and also retard the hydrogen evolution reaction.  $E_{\text{corr}}$  values was shifted towards more negative potential which is a necessary to quote the inhibitive action of inhibitor and to classify an inhibitor into an anodic, a cathodic, or mixed type. In our study, maximum displacement in  $E_{\text{corr}}$  value was around 38.5 mV corrosion potential, indicates that the studied inhibitors (PLO & PLE) act as mixed-type inhibitor [36].

### 3.6. Electrochemical impedance spectroscopy measurements

To gain supplementary knowledge on corrosion effect of mild steel in acidic media, in the presence and the absence of PLO and PLE. Electrochemical Impedance Spectroscopy (EIS) has been investigated at 303 K after 30 min of immersion. Nyquist plots recorded for steel electrode in 0.5 M  $\text{H}_2\text{SO}_4$  solution and containing various concentrations of PLO and PLE are shown in Fig. 2. It is obvious from the Fig. 2 that the Nyquist plots do not yield perfect semicircles as expected from the EIS theory. The deviation from ideal semicircle was generally attributed to the frequency dispersion [37] as well as to the inhomogenities of the surface and mass transport resistant [38]. It can be also observed from Fig. 2 that the size of the capacitive semicircle in the presence of inhibitors is larger than the size of the capacitive semicircle in the absence of these inhibitors. This fact is attributed to the inhibition effects of *P. lentiscus* inhibitors. Table 6 shows the charge-transfer resistance ( $R_t$ ), the double layer capacitance ( $C_{\text{dl}}$ ) and the frequency ( $f_m$ ) at which the imaginary component of the impedance is maximal ( $-Z_{\text{max}}$ ) are found as represented in equation:

$$C_{\text{dl}} = \frac{1}{2\pi \cdot f_m \cdot R_t} \quad (4)$$



**Figure 3.** Nyquist plots for steel electrode in 0.5 M  $\text{H}_2\text{SO}_4$  containing different concentrations of *P. lentiscus* after 30 min of immersion.

The impedance parameters data cited in Table 6 show that the values of inhibition's efficiency augment with inhibitor concentration at a maximum value 81.9% and 91.3% for PLO and PLE respectively at 2 g/L.

The values of  $E_R$  % were calculated by the equation as follows:

$$E_{\text{EIS}} \% = \left( 1 - \frac{R_t}{R'_t} \right) \times 100 \quad (5)$$

**Table 6** Impedance parameters evaluated from Nyquist plots for steel in acid at various contents of PLO and PLE respectively

Compounds	Conc. (g/l)	$R_t$ (Ohm.cm <sup>2</sup> )	$f_{max}$ (Hz)	$C_{dl}$ (μF.cm <sup>-2</sup> )	$E_{EIS}$ (%)
Blank	1M	17	50	187	-
PLO	0.25	55	31	92	69
	0.5	63	31	80	73
	1	76	25	83	77
	2	83	25	76	79
PLE	0.25	65	25	97	73
	0.5	77	25	82	78
	1	103	20	77	83
	2	121	20	65	85

### 3.7. Effect of temperature

It is well known that the temperature is one factor that can influence the behavior of a material in a corrosive environment, and can modify the interaction between the mild steel and the acid medium such as rupture, desorption of inhibitor and the decomposition and/or rearrangement of inhibitor [39]. Then the study of the influence of this factor will become a prime necessity. The corrosion effect of steel in acidic solution, in the presence and the absence inhibitors, is studied by the electrochemical impedance spectroscopy (EIS) at 303 K after 30 min of immersion. This study aims to determine the activation energy, enthalpy and entropy of activation of the corrosion process and thus provides information on the mechanism of inhibition. The corresponding data are exposed in Table 6. In order to search out information about temperature effect on the corrosion inhibition property of *P. lentiscus* inhibitors. Gravimetric experiments were conducted during 1h of immersion in the temperature range of 313–343 K. The corresponding results are listed in Table 7.

**Table 7** Effect of temperature on mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> after 1h of immersion in the presence and absence of 2 g/L of PLO & PLE

	Temp. (K)	$W_{cor}$ (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	$\eta_{wl}$ (%)
Blank	313	0.89	-
	323	1.35	-
	333	2.85	-
	343	5.83	-
PLO	313	0.241	63.9
	323	0.564	46.4
	333	1.376	32.1
	343	4.059	18.2
PLE	313	0.320	72.9
	323	0.723	58.1
	333	1.933	38.8
	343	4.766	30.3

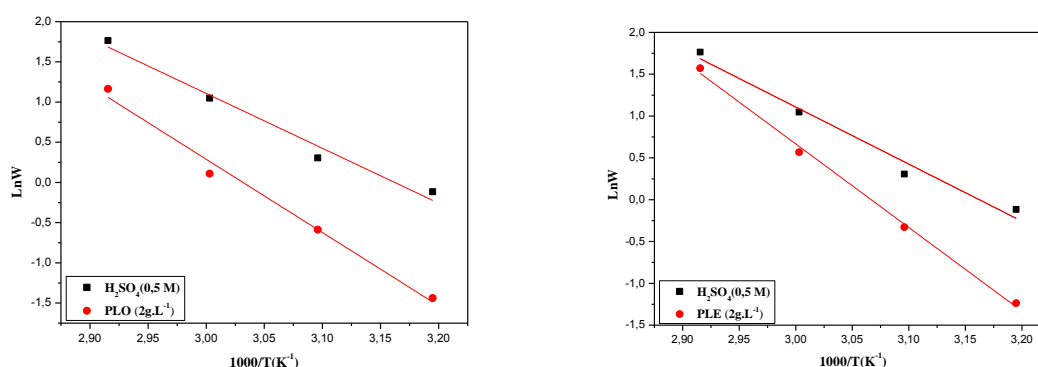
Data of comparative study given in the Table 7 show that the corrosion rate distinctly increases with rise in temperature in both stabilized solutions and inhibited, while the efficiency of inhibiting PLO and PLE products decreases to reach a value of 18.2% and 30.3% at 343 K for PLO and PLE at 1h immersion period. On the other hand, the gradually decrease on inhibition efficiency with temperature can be justified by the decrease of the strength of adsorption processes at high temperature [40]. To obtain the activation energy of the corrosion process and elucidate the inhibition properties of inhibitors, the kinetic model was used as a most practical model. The activation parameters for the corrosion process of mild steel in the absence and presence of different concentrations of *P. lentiscus* were calculated from Arrhenius Eq. (5) and transition state Eq. (6) in the temperature range from 313 to 343 K [39]:

$$\ln W = \ln A - \frac{E_a}{RT} \quad (6)$$

where  $E_a$  represents the apparent activation energy,  $R$  gas constant,  $T$  the absolute temperature,  $A$  the pre-exponential factor and  $W$  the corrosion rate, obtained from the weight loss method.

$$\ln W = \left[ \ln \left( \frac{RT}{Nh} \right) + \left( \frac{\Delta S_a^\circ}{R} \right) \right] - \frac{\Delta H_a^\circ}{RT} \quad (7)$$

Where  $N$  is the Avogadro's number and  $h$  is the Planck's constant.



**Figure 4.** Plots of  $\ln W$  versus  $1/T$  for 2 g/L of PLO and PLE in 0.5 M  $H_2SO_4$ .

Plots of logarithm of  $W$ , with reciprocal of absolute temperature ( $1/T$ ) for mild steel are shown in Fig 3. Values of apparent activation energy  $E_a$  of various concentrations of PLE and PLO were determined from the slopes of  $\ln(W)$  versus  $1000/T$  plots. The linear regression coefficients are close to 1, signifying that corrosion of mild steel in 0.5 M  $H_2SO_4$  can be elucidated using the kinetic model. Careful inspection of the data in Table 8 show that  $E_a$  increases slightly in the presence of PLO and PLE, suggesting that the inhibitory mechanism of adsorption in 0.5 M  $H_2SO_4$  is of type physisorption. Generally, the addition of compounds to the corrosive solution is accompanied by an increase in activation energy value when compared to the blank, which may often be interpreted as a sign for the development of an adsorptive film by a physical (electrostatic) mechanism [41, 42]. Moreover we can remark that the  $\Delta H_a$  values obtained from the slopes of plots  $\log (W/T)$  vs  $f(1/T)$  and those determined from the equation (7) are in good agreement. Consequently, denoting that the corrosion process is a unimolecular reaction as it is characterized by the following equation:

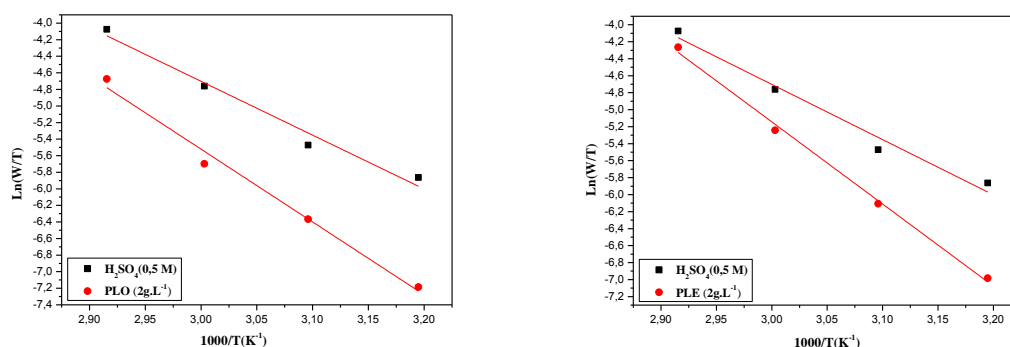
$$E_a = \Delta H_a - RT \quad (8)$$

Analyzing of kinetic-thermodynamic parameters ( $E_a$ ,  $\Delta H_a$  and  $\Delta S_a$ ) cited in Table 8 reveal that the positive values of  $\Delta H_a$  reflect the endothermic nature of metal dissolution process [36]. On comparing the values

of  $\Delta S_a$  in Table 8, indicates that  $\Delta S_a$  is more positive in presence of the studied inhibitors (PLO & PLE) compared to blank solution, implying that the activated complex is the rate-determining step, rather than the dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex and signifying that the dissolution reaction will be more blocked sites from the metal surface[43]

**Table 8:** kinetic-thermodynamic parameters for steel in 0.5 M  $H_2SO_4$  in the absence and presence of 2g/l of PLE&PLO

Compounds	$E_a$	$\Delta H_a$ k j.mol <sup>-1</sup>	$\Delta S_a$ j.K <sup>-1</sup> .mol <sup>-1</sup>	$\Delta H_a - RT$
Blank	56.77	54.04	-74.48	2.73
PLExtract	81.00	78.28	-5.16	2.72
PL Oil	83.40	80.67	0.00	2.73



**Figure 5.** Variation of  $\ln(W/T) \sim f(10^3/T)$  of steel in 0.5 M  $H_2SO_4$  with and without 2 g/L of (PLE or PLO).

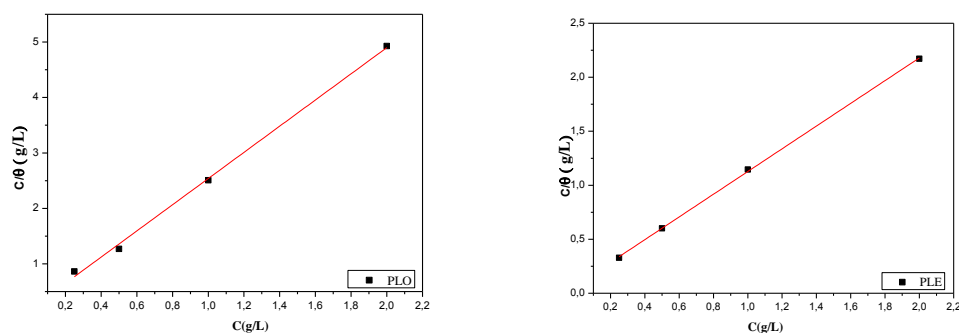
### 3.8. Adsorption isotherm

As known, organic molecules minimize metal corrosion by adsorption at the metal / solution interface. Indeed, adsorption isotherms are frequently used to understand the adsorption process. Langmuir adsorption isotherm was found as the most frequently used adsorption isotherm, which can provide a best description of the adsorption behavior of the investigated inhibitors. The Langmuir isotherm follows the equation (8)[44]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (9)$$

$$\text{With } K = \frac{1}{55.5} \cdot \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (10)$$

Where C is the concentration of inhibitor,  $\theta$  the portion of the surface covered which have been calculated by  $\eta_{WL}(\%) / 100$ , k the equilibrium constant,  $\Delta G_{ads}$  is the standard free energy of adsorption reaction, and the value of 55.5 is the concentration of water in the solution in mol/L. Plots of the ratio  $C/\theta$  as function of C for PLE and PLO, respectively. Are shown in Fig. 5.



**Figure 6.** Langmuir adsorption isotherm of PLE and PLO on the mild steel.

## 4. Conclusion

*Pistacia lentiscus* was proved to be an effective green corrosion inhibitor of mild steel at different temperatures in 0.5 M  $H_2SO_4$  solution. The polarization studies revealed that PLO and PLE act as mixed-type inhibitors of corrosion. The inhibition efficiency of PLE and PLO increases with the increase of inhibition concentration. The adsorption of the *P. lentiscus* compounds on the mild steel surface in 0.5 M  $H_2SO_4$  solution obeys Langmuir adsorption model. *P. lentiscus* inhibitors being natural and environmentally benign products, they can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.

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